



Paleoceanography

RESEARCH ARTICLE

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Key Points:

- Coral biomineralization confounds geochemical temperature proxies based on single element/Ca ratios
- U/Ca ratios track the calcifying fluid variations that distort the temperature dependence of Sr/Ca
- Coral Sr/Ca and U/Ca ratios used in tandem improve accuracy of seawater temperature reconstructions

Supporting Information:

- Supporting Information S1
- Data Set S1

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Coral Sr-U thermometry

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Abstract Coral skeletons archive past climate variability with unrivaled temporal resolution. However, extraction of accurate temperature information from coral skeletons has been limited by “vital effects,” which confound, and sometimes override, the temperature dependence of geochemical proxies. We present a new approach to coral paleothermometry based on results of abiogenic precipitation experiments interpreted within a framework provided by a quantitative model of the coral biomineralization process. DeCarlo et al. (2015a) investigated temperature and carbonate chemistry controls on abiogenic partitioning of Sr/Ca and U/Ca between aragonite and seawater and modeled the sensitivity of skeletal composition to processes occurring at the site of calcification. The model predicts that temperature can be accurately reconstructed from coral skeleton by combining Sr/Ca and U/Ca ratios into a new proxy, which we refer to hereafter as the Sr-U thermometer. Here we test the model predictions with measured Sr/Ca and U/Ca ratios of 14 *Porites* sp. corals collected from the tropical Pacific Ocean and the Red Sea, with a subset also analyzed using the boron isotope ($\delta^{11}\text{B}$) pH proxy. Observed relationships among Sr/Ca, U/Ca, and $\delta^{11}\text{B}$ agree with model predictions, indicating that the model accounts for the key features of the coral biomineralization process. By calibrating to instrumental temperature records, we show that Sr-U captures 93% of mean annual temperature variability (26–30°C) and has a standard deviation of prediction of 0.5°C, compared to 1°C using Sr/Ca alone. The Sr-U thermometer may offer significantly improved reliability for reconstructing past ocean temperatures from coral skeletons.

1. Introduction

Since 1900, global mean surface temperatures have increased at an average rate of $\sim 0.08^\circ\text{C}$ per decade, and state-of-the-art general circulation models project further warming of 1–4°C by the end of this century in response to anthropogenic greenhouse gas (GHG) emissions [Meehl et al., 2012; Stocker et al., 2013]. These projections depend in large part on estimates of “climate sensitivity,” the sensitivity of Earth’s temperature to a doubling of atmospheric CO_2 , and there is substantial uncertainty in these estimates. Natural oscillations in atmospheric and oceanic circulation occurring on interannual (e.g., El Niño–Southern Oscillation), multidecadal (e.g., Pacific Decadal Oscillation), and centennial (e.g., the Little Ice Age) timescales can partially obscure climate sensitivity, and how these modes of variability interact with, and possibly change, under GHG forcing remain uncertain [Wittenberg, 2009; Stevenson et al., 2012; Emile-Geay et al., 2013; Li et al., 2013; Meehl et al., 2014]. Multicentury long records of temperature can help to resolve these issues by enabling characterization of internal variability and isolation of secular temperature trends driven by external forcing (e.g., GHGs).

Direct observations of temperature, however, extend back only as far as the middle of the nineteenth century [Smith et al., 2008]. Furthermore, in regions such as the central tropical Pacific Ocean, where sparse observations exist prior to 1950 [Giese and Ray, 2011], estimates of twentieth century warming vary up to a factor of 2 [Nurhati et al., 2011; Solomon and Newman, 2012; Emile-Geay et al., 2013]. These limits to the length and reliability of instrumental records make it difficult to constrain the range of natural variability, the degree of twentieth century warming, and the climate sensitivity to GHG forcing. Accurate proxy temperature reconstructions offer the only way to extend the relatively short observational period further into the past and overcome the limitations of instrumental temperature records.

The skeletons of long-lived reef-building corals are a promising archive of this information. Distributed across the tropics at shallow water depths, corals are exposed to the sea surface temperature (SST) and accrete their

skeletons in alternating high- and low-density bands that provide intrinsic, high-resolution time markers extending hundreds of years into the past [Buddemeier *et al.*, 1974]. As corals grow, the geochemistry of their skeletal aragonite is sensitive to fluctuations in environmental conditions, including temperature. The most common coral-based temperature proxy currently in use is the Sr/Ca thermometer, which exploits the inverse relationship between Sr/Ca and water temperature [Kinsman and Holland, 1969; Smith *et al.*, 1979; Gaetani and Cohen, 2006; DeCarlo *et al.*, 2015a]. Typically, Sr/Ca ratios are first calibrated with modern instrumental SST records to establish a coral-specific Sr/Ca-temperature relationship and then applied downcore to the older skeleton of the same coral, or in some cases to fossil corals, in order to reconstruct past SST [Smith *et al.*, 1979; Felis *et al.*, 2009; Hereid *et al.*, 2013; Tierney *et al.*, 2015; Toth *et al.*, 2015].

However, problems arise because SST is not the only factor that influences coral Sr/Ca. The biomineralization process affects Sr/Ca ratios and can do so independently of any changes in temperature. These biological influences are known as “vital effects” and are obvious in the comparison between coral and abiogenic aragonites. The temperature dependence of Sr/Ca in coral skeleton (-0.05 to -0.08 mmol mol⁻¹ Sr/Ca per °C) is significantly stronger than that of abiogenic aragonite (-0.039 to -0.044 mmol mol⁻¹ Sr/Ca per °C) [Cohen *et al.*, 2002; Gaetani and Cohen, 2006; Gaetani *et al.*, 2011; DeCarlo *et al.*, 2015a], and Sr/Ca-temperature relationships derived for different corals can vary widely. For *Porites* corals, a given Sr/Ca ratio can correspond to a range of temperatures in excess of 10°C depending on which calibration equation is applied [Corrège, 2006; Gaetani *et al.*, 2011]. The influences of vital effects on Sr/Ca ratios are also borne out in coral-based SST reconstructions, which repeatedly fail to capture observed temperature trends [Grove *et al.*, 2013; Storz *et al.*, 2013; Karnauskas *et al.*, 2015; Alpert *et al.*, 2016] and often decouple from observed SST by > 4°C [Marshall and McCulloch, 2002; Felis *et al.*, 2009; Wu *et al.*, 2014].

Evidence suggests that these Sr/Ca vital effects arise because corals accrete their skeleton within an isolated calcifying space [Cohen *et al.*, 2006; Gaetani and Cohen, 2006]. As aragonite crystals nucleate from the fluid within this space, the elemental composition of the fluid changes. Element ratios that are elevated in aragonite relative to the fluid (e.g., Sr/Ca) become progressively lower in the fluid as precipitation proceeds. This is known as Rayleigh fractionation [Cohen *et al.*, 2006; Gaetani and Cohen, 2006]. At a given temperature, the Sr/Ca ratio of the aragonite will monotonically decrease as precipitation proceeds, in response to changes in the Sr/Ca ratio of the calcifying fluid. Fluctuations in calcifying fluid carbonate ion concentration ([CO₃²⁻]) likely drive variations in the amount of aragonite precipitation and thus cause fluctuations in the magnitude of the Rayleigh fractionation vital effect [Cohen *et al.*, 2009; Gagnon *et al.*, 2013]. Accurate coral-based temperature proxies must therefore account for this process in order to isolate the temperature component of geochemical variability in the skeleton.

Abiogenic aragonite precipitation experiments showed that U/Ca ratios of aragonite precipitated from seawater decrease as carbonate ion concentrations increase [DeCarlo *et al.*, 2015a], and thus, U/Ca ratios have potential to account for the vital effects that influence Sr/Ca ratios. Here we use coral Sr/Ca and U/Ca ratios interpreted within the context of the biomineralization model developed by DeCarlo *et al.* [2015a] to test the hypothesis that Sr/Ca and U/Ca ratios can be used in tandem to accurately reconstruct past seawater temperature. We use data from 14 corals collected in the tropical Pacific Ocean and the Red Sea, for which instrumental temperature data are available for comparison. In a subset of these corals, we also measured boron isotopic composition (a proxy for pH) to test our hypothesis that vital effects in coral Sr/Ca ratios arise from processes occurring during biomineralization.

2. Methods

2.1. Coral Records

Coral skeleton cores were collected from massive *Porites* sp. colonies using underwater pneumatic drills. Two cores were collected from the central Red Sea near Jeddah, Saudi Arabia, two from Palmyra Atoll, four from Jarvis Island, and six in the Republic of Palau (Figure 1). The mean annual temperatures at which each coral lived were acquired for time periods coincident with element ratio measurements using the NOAA-Optimum Interpolation (OI) SST data set [Reynolds *et al.*, 2002]. Temperature was compared between NOAA-OI and in situ temperature loggers deployed on each reef at the water depths of coral samples, and a correction was applied to NOAA-OI to account for any mean bias in temperature during overlapping time periods with the in situ loggers (Figure 1).

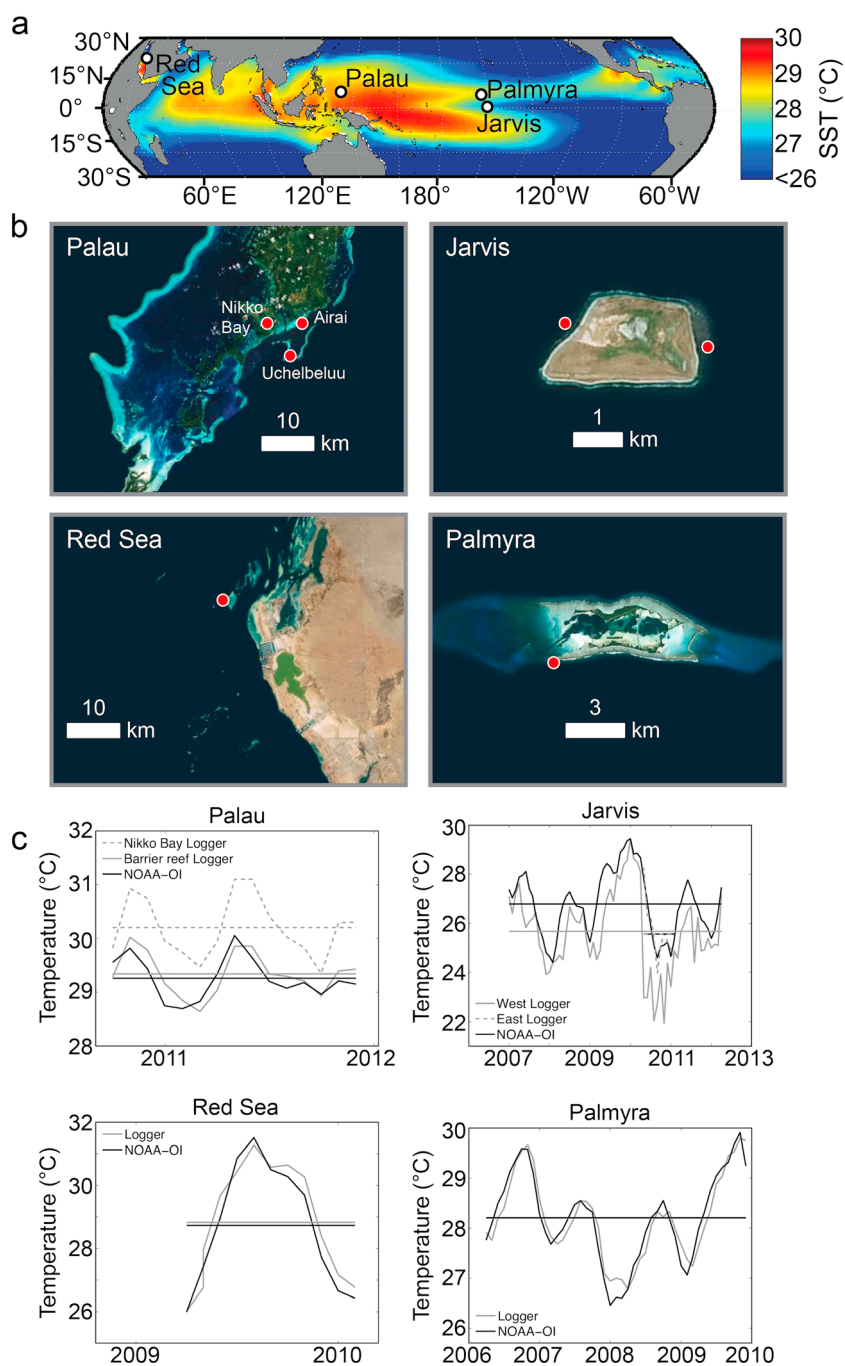


Figure 1. Coral sampling locations and sea surface temperatures. (a) Map of climatological mean (1971–2000) sea surface temperature (SST) from the NOAA-OI data set, with coral reef sampling locations indicated by white dots. (b) Satellite images of each reef, with locations of coral sampling indicated by red dots. (c) Comparisons between NOAA-OI and in situ logger temperatures for each coral sampling location. Horizontal bars indicate mean temperature for each location.

Coral cores were scanned with a Siemens Volume Zoom Spiral Computerized Tomography (CT) scanner to determine skeletal density. Annual density banding was used to develop an age model for each coral (Figure 2). Slabs were cut from cores with a water-cooled diamond wafering blade and cleaned for 15 min in an ultrasonic bath filled with 18.2 MΩ deionized water before drying at 60°C for at least 24 h. Subsamples of approximately 100 μg were drilled from slabs with a fine-tipped, diamond-impregnated drillbit at 0.5 to 1.25 mm (approximately monthly) resolution. Sampling followed primary growth axes, tracking the growth paths of corallites.

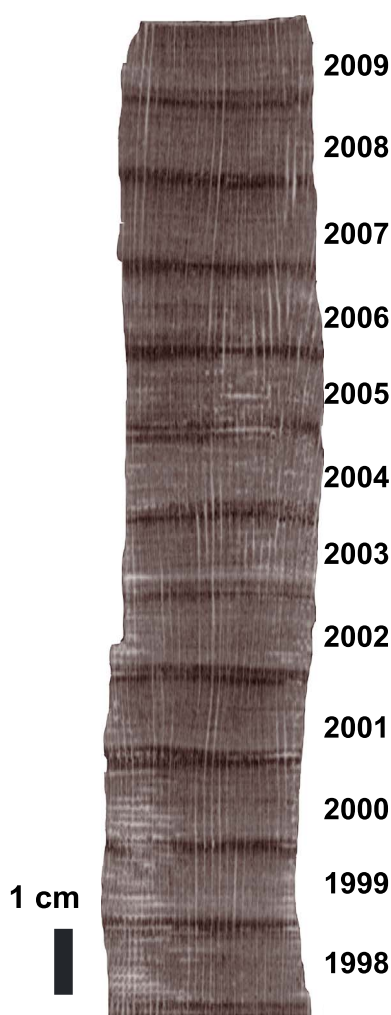


Figure 2. Computerized tomography (CT) scan of Palmyra 3 coral. Light (dark) shading indicates relatively high (low) density skeleton. The timescale is derived from annual density banding, visible as approximately horizontal alternating low- and high-density bands.

2.2. Trace Elements

Coral powders were dissolved in 5% trace metal grade nitric acid and counts of ^{48}Ca , ^{88}Sr , and ^{238}U were measured in low resolution on a Thermo Element 2 inductively coupled plasma mass spectrometer (ICP-MS) at Woods Hole Oceanographic Institution. External precision (one relative standard deviation) was 0.4% for Sr/Ca and 0.8% for U/Ca, determined via repeated measurements of a secondary coral standard treated as a sample. Jarvis data are reported in Alpert *et al.* [2016]. Element ratio measurements were standardized to the JCp-1 coral standard [Okai *et al.*, 2002], which has nominal Sr/Ca and U/Ca ratios of $8.838 \pm 0.042 \text{ mmol mol}^{-1}$ and $1.192 \pm 0.045 \text{ } \mu\text{mol mol}^{-1}$, respectively [Hathorne *et al.*, 2013]. JCp-1 analyses bracketed every eight sample analyses. Sr/Ca ratios were also measured repeatedly in standard materials derived from fish otoliths [Yoshinaga *et al.*, 2000; Sturgeon *et al.*, 2005] and the NBS-19 limestone [Fernandez *et al.*, 2011] to ensure consistency of our Sr/Ca calibrations. As reported in Alpert *et al.* [2016], the batch of JCp-1 used in this study was compared to High Purity Standards single element standards gravimetrically mixed to simulate coral skeleton (40 ppm Ca with variable concentrations of Mg, Sr, Ba, and U). Three aliquots of JCp-1 powder were dissolved and each analyzed in duplicate with resulting mean $\pm 1\sigma$ for Sr/Ca of $8.87 \pm 0.03 \text{ mmol mol}^{-1}$ and U/Ca of $1.23 \pm 0.01 \text{ } \mu\text{mol mol}^{-1}$.

2.3. Boron Isotopes

Two pairs of corals, each pair collected from a single reef in Palau, were analyzed for boron isotopic composition. $\delta^{11}\text{B}$ was measured in splits of the same samples used for Sr/Ca and U/Ca analyses following the methods of Foster [2008] and Foster *et al.* [2013]. Briefly, $\delta^{11}\text{B}$ splits were oxidatively cleaned at 80°C in 1% H_2O_2 (buffered with 0.1 M NH_4OH) in the clean lab of the University of Southampton. Oxidatively cleaned samples were then subjected to a weak acid leach and dissolved in a minimum volume of 0.5 M HNO_3 , and boron was then separated from the

dissolved sample using Amberlite IRA 743 anion exchange resin in 20 μL microcolumns. The boron isotopic composition was determined using a Thermo Scientific Neptune multicollector ICP-MS at the University of Southampton normalized against National Institute of Standards and Technology Standard Reference Material 951. The long term precision (following Henehan *et al.* [2013]) was better than $\pm 0.21\text{‰}$ at 95% confidence, and during the course of this study repeat analysis of JCp-1 gave $\delta^{11}\text{B}$ of $24.2 \pm 0.2\text{‰}$ at 95% confidence. Calcifying fluid pH was calculated from measured $\delta^{11}\text{B}_{\text{coral}}$ as $\text{pH} = \text{pK}_B - \log \left(\frac{\delta^{11}\text{B}_{\text{seawater}} - \delta^{11}\text{B}_{\text{coral}}}{\delta^{11}\text{B}_{\text{seawater}} - \alpha_B \delta^{11}\text{B}_{\text{coral}} - 1000(\alpha_B - 1)} \right)$ following Zeebe and Wolf-Gladrow [2001] where α_B is equal to 1.0272 [Klochko *et al.*, 2006], pK_B is estimated from temperature and salinity based on Dickson [1990], and $\delta^{11}\text{B}_{\text{seawater}}$ is assumed to be 39.6‰ (following Foster *et al.* [2010]) and representative of the calcifying fluid. For each coral we calculated the mean pH over 2008–2009 in order to facilitate comparison among corals.

2.4. Statistics

The relationship between Sr/Ca and U/Ca in our coral samples was examined using linear regression, and with analysis of covariance (ANCOVA) in which Sr/Ca is the dependent variable, U/Ca is the covariate,

and coral colony is an independent factor. ANCOVA tests the significance of Sr/Ca to U/Ca correlation in our corals, while allowing the relationship between Sr/Ca and U/Ca to vary among coral colonies. We evaluated our data with ANCOVA both including and excluding an interaction between coral colony and U/Ca (i.e., different slopes of Sr/Ca versus U/Ca for different corals). Differences in mean values of element ratios or calcifying fluid pH between corals were evaluated with two-sample *t* tests. Linear regression was used to test for correlations between coral geochemical data and temperature. Throughout this study, significance is defined as $p < 0.05$. Coral trace element and boron isotope data are reported in the supporting information.

3. Results and Discussion

3.1. Modeling Vital Effects

Vital effects on coral skeletal geochemistry are linked with the biomineralization process. Corals nucleate and grow the aragonite crystals that form their skeleton within an isolated space located beneath the calicoblastic epithelial cells [Barnes, 1970; Venn *et al.*, 2011]. Evidence from culture experiments with calcein dyes and solutions doped with biologically inert elements suggests that seawater transport into this space supplies the elements for crystallization [Gagnon *et al.*, 2012; Tambutté *et al.*, 2012]. Corals modify the carbonate chemistry of the incoming seawater—likely via alkalinity pumping [Al-Horani *et al.*, 2003; Cohen and McConnaughey, 2003; Venn *et al.*, 2011]—to induce aragonite precipitation. The modified seawater from which the aragonite crystals precipitate is referred to as the extracellular calcifying fluid (ECF). If calcification proceeds in an isolated (or semi-isolated) space, as microscopy [Venn *et al.*, 2011] and geochemical [Cohen *et al.*, 2006; Gaetani and Cohen, 2006] evidence suggests, there are critical implications for interpreting compositional variations in coral skeleton. Changes in the extent of precipitation from an isolated calcifying fluid would lead to variability of element ratios in coral skeletons as a result of Rayleigh fractionation. For many corals, more than half of the Sr/Ca variance has been attributed to such vital effects [Cohen *et al.*, 2002; Gaetani *et al.*, 2011].

To shed light on the origin of vital effects and to potentially quantify their effects on the composition of coral skeleton, we can look to covariability among multiple element ratios. The basis for a multielement approach to coral paleothermometry comes from laboratory experiments that determined the abiogenic controls on elemental partitioning between aragonite and seawater [Gaetani and Cohen, 2006; Gabitov *et al.*, 2008]. Modeling studies placed abiogenic partitioning of multiple elements within a coral biomineralization framework [Cohen *et al.*, 2006; Cohen and Gaetani, 2010; Gagnon *et al.*, 2012], including the development of the “Rayleigh-Based Multi-Element” thermometer [Gaetani *et al.*, 2011]. Subsequent coral culture and modeling studies identified the importance of carbonate chemistry changes occurring within the ECF on the elemental composition of the skeleton [Cohen *et al.*, 2009; Gagnon *et al.*, 2013; Tanaka *et al.*, 2015]. Recently, DeCarlo *et al.* [2015a] conducted laboratory precipitation experiments that characterized the abiogenic carbonate chemistry and temperature controls on Sr/Ca and U/Ca partitioning between aragonite and seawater. Previous studies consistently report positive correlations between coral Sr/Ca and U/Ca ratios [Cardinal *et al.*, 2001; Hendy *et al.*, 2002; Quinn and Sampson, 2002; Fallon *et al.*, 2003; Sinclair *et al.*, 2006; Felis *et al.*, 2009, 2012; Jones *et al.*, 2015]. However, correlations between Sr/Ca and U/Ca are not found in experimentally precipitated abiogenic aragonite, in which Sr/Ca is controlled by temperature and is insensitive to $[\text{CO}_3^{2-}]$, whereas U/Ca is controlled by $[\text{CO}_3^{2-}]$ but is insensitive to temperature [DeCarlo *et al.*, 2015a]. The correlations between Sr/Ca and U/Ca in coral skeletons must, therefore, derive from processes occurring during biomineralization.

Quantitative, geochemical models of the coral biomineralization process provide a framework within which the environmental drivers of variability in skeletal composition (e.g., Sr/Ca sensitivity to SST) can be distinguished from vital effects that arise during biomineralization (e.g., influence of Rayleigh fractionation on Sr/Ca). DeCarlo *et al.* [2015a] developed a forward biomineralization model that successfully predicts Sr/Ca and U/Ca ratios of coral skeleton. Seawater exchange, alkalinity pumping, and aragonite precipitation modify the elemental composition of the ECF (Figure 3). Together, these processes influence the Sr/Ca and U/Ca ratios of the skeleton via Rayleigh fractionation and changes in the ECF $[\text{CO}_3^{2-}]$. This combination of factors produces a positive correlation between coral skeleton Sr/Ca and U/Ca ratios at a single temperature, such that a given coral Sr/Ca ratio does not correspond to a unique temperature (Figure 3). However, the modeling results also suggest a new approach for deriving temperature from coral skeletons.

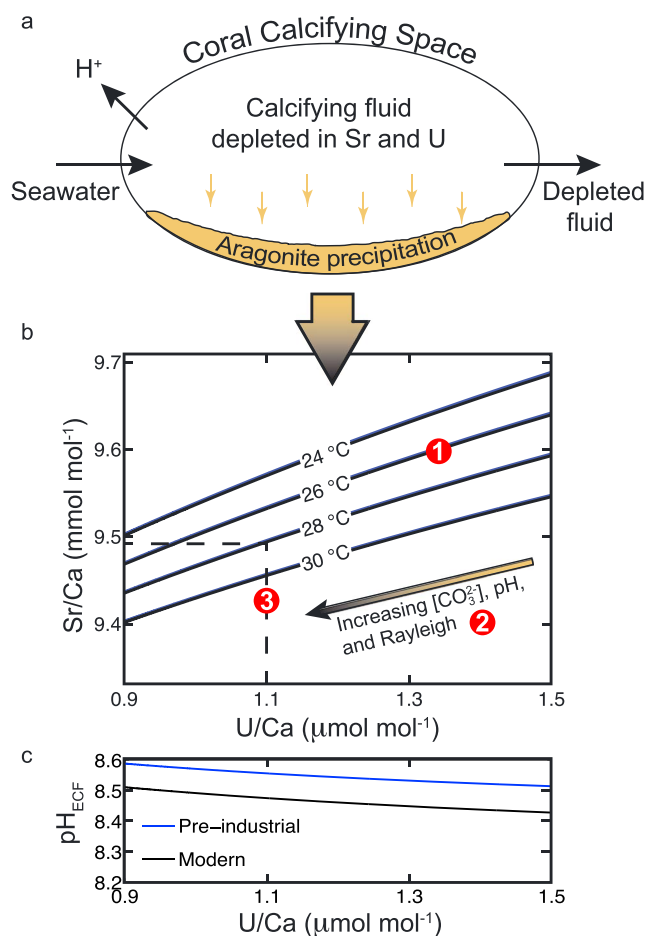


Figure 3. Coral biomineralization model. (a) Schematic diagram of semi-isolated coral calcifying space where the fluid in the space is supplied by seawater and elemental concentrations of the fluid are depleted relative to seawater as aragonite precipitates. Removal of protons (H^+) from the fluid represents alkalinity pumping. (b) The model of DeCarlo *et al.* [2015a] is evaluated between 24°C and 30°C (solid black lines, each representing the relationship between Sr/Ca and U/Ca at a specific temperature) and plotted for U/Ca ratios consistent with *Porites* coral skeleton (0.9 to 1.5 μ mol mol⁻¹). Red circles indicate the three predictions of the model that we test with coral data: (1) skeleton Sr/Ca and U/Ca ratios are positively correlated, (2) increasing Rayleigh fractionation, combined with increasing ECF pH and $[CO_3^{2-}]$, decreases both skeleton Sr/Ca and U/Ca ratios, and (3) at a specific skeleton U/Ca ratio (dashed line), Sr/Ca depends only upon temperature. (c) Predicted calcifying fluid pH and coral skeleton U/Ca ratio at salinity 35 and temperature of 25°C, and assuming ambient seawater total alkalinity of 2300 μ eq kg⁻¹, and $[CO_3^{2-}]$ of preindustrial (blue) and today (black) based on Feely *et al.* [2009]. While the absolute pH_{ECF} at a particular U/Ca ratio is sensitive to ambient seawater $[CO_3^{2-}]$, the model consistently predicts increasing pH_{ECF} with decreasing Sr/Ca and U/Ca ratios. Critically though, seawater $[CO_3^{2-}]$ has little influence on $Sr-U$ temperature sensitivity, and the industrial $[CO_3^{2-}]$ change would shift the isolines in Figure 3b by the equivalent of only $\sim 0.03^\circ\text{C}$ (note that the blue and black lines representing the two $[CO_3^{2-}]$ scenarios are partially overlapping in Figure 3b).

U/Ca ratios can be used in tandem to accurately reconstruct temperature. In particular, here we test the prediction that the Sr/Ca ratio of each coral corresponding to a specific U/Ca ratio correlates with temperature (Figure 3). To do this, we select the median U/Ca ratio among all of our coral data (1.1 μ mol mol⁻¹), and

Since U/Ca is sensitive to Rayleigh fractionation—through variations in $[CO_3^{2-}]$ —but not to temperature, a single U/Ca ratio can serve as a benchmark with which to investigate variability in other element ratios independent of vital effects driven by Rayleigh fractionation. Comparing Sr/Ca ratios that correspond to a single U/Ca ratio should, therefore, isolate the temperature component of the Sr/Ca signal (Figure 3).

3.2. Development of Sr-U Thermometry

The implication of the biomineralization model is that Sr/Ca and U/Ca ratios in coral skeleton can be combined to accurately reconstruct past seawater temperature. Here we use our coral Sr/Ca , U/Ca , and $\delta^{11}\text{B}$ data to test predictions from the biomineralization model (Figure 3). The first prediction of the model is that Sr/Ca and U/Ca are positively correlated within the skeleton of each coral colony. We found that Sr/Ca is significantly positively correlated with U/Ca (ANCOVA including interaction between coral colony and U/Ca , $r^2 = 0.86$) across all of our corals (Figures 4 and 5). According to the model, corals that experience the same temperature may have different Sr/Ca ratios, but we expect that any differences in Sr/Ca among such corals will be positively correlated with U/Ca and inversely correlated with pH_{ECF} (Figure 3). We tested this prediction using corals from Palau that have significantly different Sr/Ca ratios even though they experienced the same temperatures (Figure 4 and supporting information Figure S1). Within each pair of corals collected from a single reef and sampled over the same time period (i.e., that experienced the same temperatures), the pH_{ECF} is significantly higher, and the U/Ca ratio is significantly lower, in the coral with lower Sr/Ca (Figure 4), consistent with the model prediction (Figure 3).

The key prediction of the model for paleothermometry is that Sr/Ca and

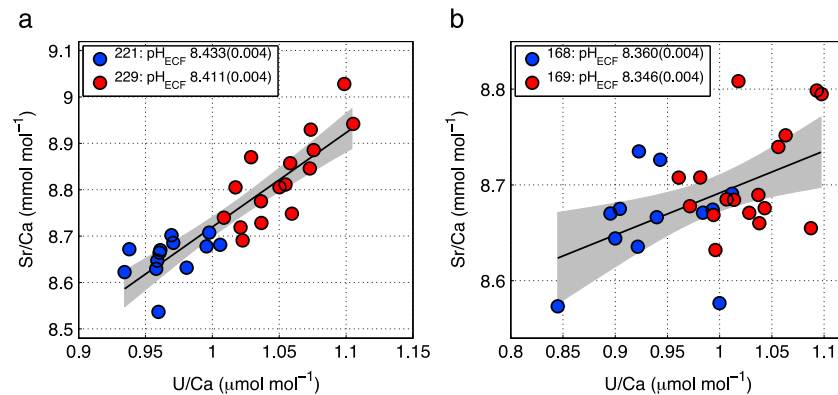


Figure 4. Vital effects in two pairs of corals, each pair collected from a single reef in Palau and sampled over the same time period (2008–2009). Property-property plots of Sr/Ca and U/Ca ratios from corals collected in (a) Uchelbeluu (corals “221” and “229”) and (b) Nikko Bay (corals “168” and “169”). Sr/Ca and U/Ca ratios of corals collected from a single reef are positively correlated. Within each pair of corals from a single reef, lower Sr/Ca and U/Ca ratios are correlated with elevated pH_{ECF} . The pH_{ECF} is reported as the mean with the number in parentheses indicating the standard error of the mean. Solid black lines with gray bounds indicate least squares regression and 95% confidence interval between Sr/Ca and U/Ca ratios. Note that the scales are different between the panels in order to aid interpretation of the plots. Time series plots of these data are displayed in supporting information Figure S1.

we use the correlations between Sr/Ca and U/Ca to estimate the Sr/Ca ratio, for each coral, that corresponds to this median U/Ca ratio. We first regress Sr/Ca with U/Ca, separately for each coral:

$$\widehat{\text{Sr/Ca}} = m_i(\text{U/Ca}) + b_i, \quad (1)$$

where $\widehat{\text{Sr/Ca}}$ is the estimated Sr/Ca ratio from a given U/Ca ratio, m_i is the slope and b_i is the intercept of ordinary least squares regression performed using the data of a single coral i with Sr/Ca as the dependent variable and U/Ca the independent variable. We then define Sr-U for each coral as the estimated Sr/Ca ratio at the median U/Ca ratio:

$$\text{Sr-U}_i = m_i(1.1) + b_i, \quad (2)$$

where a single Sr-U_{*i*} value is estimated for each coral, i . Sr-U from the 14 corals is significantly correlated with mean annual temperature ($r^2 = 0.93$, Figure 5 and Table 1), in agreement with the prediction of the biomineralization model. Temperature is predicted from Sr-U according to the following calibration equation (± 1 standard error of coefficients):

$$\text{Temperature } (^{\circ}\text{C}) = (-11 \pm 1)(\text{Sr-U} - 9) + (28.1 \pm 0.1), \quad (3)$$

where 9 is subtracted from Sr-U to center the regression about zero. Whereas equations (1) and (2) are defined independently for each colony (i.e., the regression between Sr/Ca and U/Ca is based on a particular coral record), the temperature sensitivity of Sr-U in equation (3) is calibrated with all 14 corals in our data set. The standard deviation of prediction of mean temperature for Sr-U is $\pm 0.5^{\circ}\text{C}$ and the root-mean-square error between observed and predicted temperature is 0.4°C , approximately half of the uncertainty based on Sr/Ca alone (Figure 5).

In our ANCOVA, the intercept of the relationship between Sr/Ca and U/Ca varies greatly among coral colonies (explaining 58% of total Sr/Ca variance). While differences in the slope of the Sr/Ca and U/Ca relationship (i.e., interaction between coral colony and U/Ca) are significant, the slopes vary only slightly (explaining $\sim 1\%$ of total Sr/Ca variance). This means that most (84%) of Sr/Ca variance is explained by regression to U/Ca with a single slope applied to all corals but with different intercepts (i.e., offsets in Sr/Ca among corals). Including the interaction term is statistically robust, but it has potentially important ramifications for applying Sr-U outside of our calibration. The strength of the correlation between Sr/Ca and U/Ca influences the ordinary least squares slope, and thus, Sr-U could be sensitive to any effect of sampling resolution on the r^2 between Sr/Ca and U/Ca. Further, if we include the interaction term, we must define Sr-U as the Sr/Ca ratio predicted at a certain U/Ca ratio, one that is within the range of our data set. Extrapolation to higher or lower U/Ca ratios would lead to small differences in the Sr/Ca to U/Ca slope among corals having a

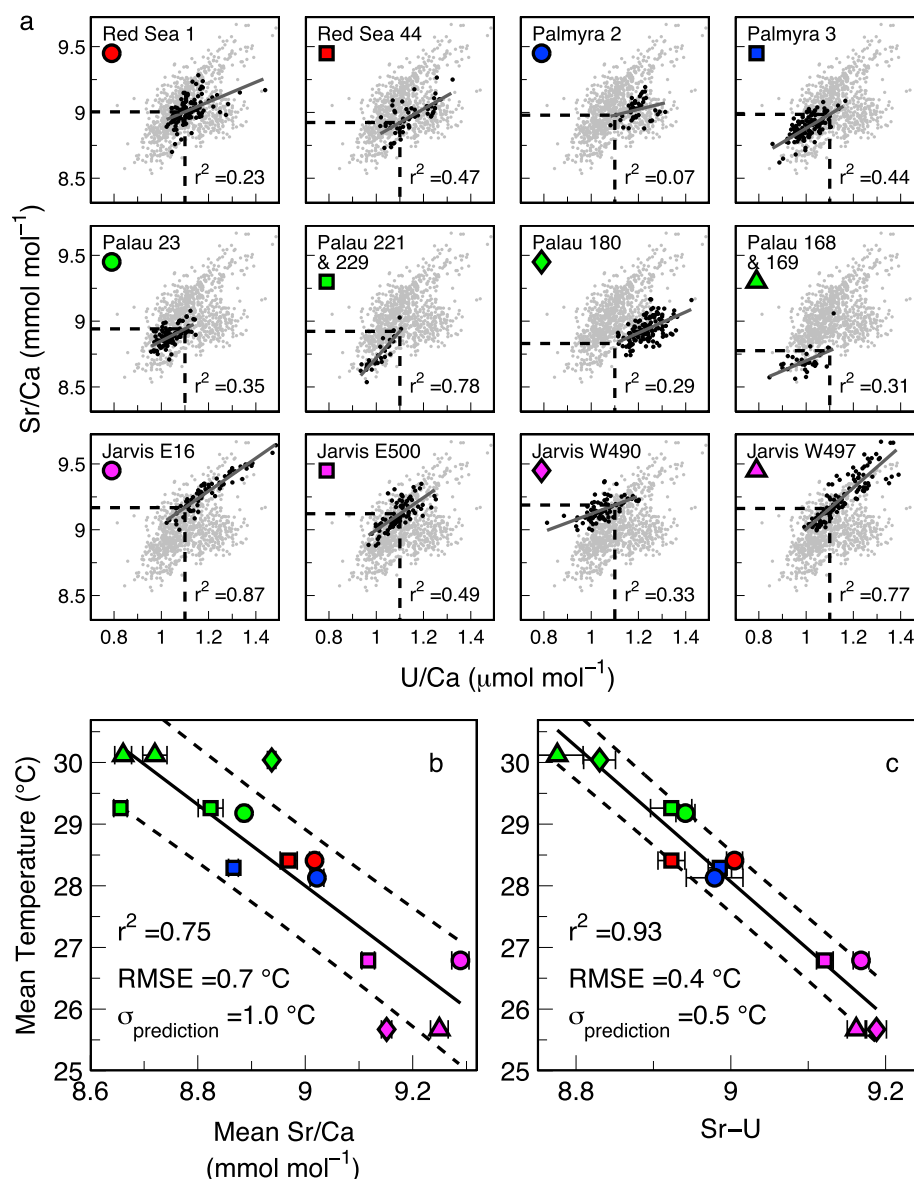


Figure 5. Calibration of the Sr-U thermometer. (a) Sr/Ca and U/Ca relationship of 14 *Porites* colonies from the Pacific Ocean and Red Sea. Each panel shows the data for a given coral in black and all other corals in light gray. The trend lines for each coral were fit by ordinary least squares regression between Sr/Ca and U/Ca (solid dark gray lines). Sr-U is the estimated Sr/Ca at U/Ca of 1.1 μmol mol⁻¹ (dashed lines). (b, c) The colored symbol below the name of each coral indicates its position on the calibration plots. Palau 221 and 229 (Uchelbeluu) and Palau 168 and 169 (Nikko Bay) data are each grouped from two separate corals collected on the same reefs because one coral from each location did not include U/Ca ratios as high as 1.1 μmol mol⁻¹ needed to define Sr-U. (b) Mean Sr/Ca and (c) Sr-U for each coral regressed with mean annual temperature. Dashed lines in Figures 5b and 5c show 1σ of prediction. Horizontal error bars in Figure 5b show standard error of mean Sr/Ca and in Figure 5c show the 1σ uncertainty of the Sr/Ca and U/Ca regression at U/Ca of 1.1 μmol mol⁻¹.

disproportionally large effect on Sr-U. Alternatively, similar results are produced when Sr-U is defined without the interaction term (i.e., the slope of Sr/Ca and U/Ca is the same for all corals), which is implemented by replacing equations (2) and (3) with equations (4) and (5), respectively:

$$\text{Sr-U}_{\text{parallel}} = \overline{\text{Sr/Ca}} - 1.1107\overline{\text{U/Ca}} \quad (r^2 = 0.84), \quad (4)$$

$$\text{Temperature (°C)} = (-10 \pm 1)(\text{Sr-U}_{\text{parallel}} - 7.7) + (28.8 \pm 0.1) \quad (r^2 = 0.91), \quad (5)$$

where overbars indicate means and Sr/Ca and U/Ca are in units of mmol mol⁻¹ and μmol mol⁻¹, respectively.

Table 1. Summary of Coral Temperature, Sr/Ca and U/Ca Correlations, Sr-U, and Sr/Ca^a

	Location	Depth (m)	Mean Temperature (°C)	r^2	m	Sr-U	Mean Sr/Ca (mmol mol ⁻¹)
<i>This study</i>							
Jarvis West W490	0.3696°S, 160.0083°W	7	25.67 (2007–2012)	0.81	1.3 (0.4)	9.19 (0.03)	9.15
Jarvis West W497	0.3689°S, 160.0081°W	16	25.67 (2007–2012)	0.64	1.9 (0.2)	9.16 (0.02)	9.25
Jarvis East 16	0.3739°S, 159.9834°W	5	26.79 (2007–2012)	0.86	1.4 (0.1)	9.17 (0.02)	9.29
Jarvis East E500	0.3715°S, 159.9823°W	5	26.79 (2007–2012)	0.49	2.2 (0.5)	9.12 (0.02)	9.12
Palmyra 2	5.8664°N, 162.1095°W	13	28.13 (2006–2010)	0.07	5 (5)	8.98 (0.07)	9.02
Palmyra 3	5.8664°N, 162.1095°W	13	28.29 (1998–2010)	0.44	2 (0.4)	8.99 (0.03)	8.89
Red Sea 1	22.0314°N, 38.8778°E	1	28.41 (1998–2009)	0.23	2.3 (0.8)	9.00 (0.02)	9.02
Red Sea 44	22.0314°N, 38.8778°E	5	28.41 (2005–2009)	0.46	1.8 (0.8)	8.92 (0.03)	8.97
Palau 23 (Airai)	7.3321°N, 134.5602°E	4	29.18 (1997–1999)	0.36	2.0 (0.5)	8.94 (0.02)	8.89
Palau 221 (Uchelbeluu) ^b	7.267°N, 134.521°E	5	29.26 (2008–2009)	0.79	2.5 (0.5)	8.92 (0.05)	8.66
Palau 229 (Uchelbeluu) ^b	7.267°N, 134.521°E	5	29.26 (2008–2009)	0.79	2.5 (0.5)	8.92 (0.05)	8.82
Palau 180 (Nikko Bay)	7.3248°N, 134.4684°E	6	30.04 (1997–1999)	0.29	2.0 (0.5)	8.83 (0.04)	8.94
Palau 168 (Nikko Bay) ^b	7.3248°N, 134.4684°E	3	30.12 (2008–2009)	0.30	1.8 (0.9)	8.78 (0.07)	8.66
Palau 169 (Nikko Bay) ^b	7.3248°N, 134.4684°E	6	30.12 (2008–2009)	0.30	1.8 (0.9)	8.78 (0.07)	8.72
<i>Literature data</i>							
Cardinal et al. [2001] Bermuda N Rocks	32.5°N, 64.67°W	24	23.0 (1971–1984)	0.67	2.1 (0.4)		
Bermuda NE Breakers	32.5°N, 64.67°W	11	22.9 (1981–1984)	0.49	1.9 (0.6)		
Quinn and Sampson [2002] New Caledonia	22.48°S, 116.47°E	3	24.7 (1968–1990)	0.52	1.6 (0.2)		
Felis et al. [2009] Japan	27.106°N, 142.194°E	6	24.3 (1982–1994)	0.88	1.6 (0.1)		

^aCoefficient of determination (r^2) and slope (m) of Sr/Ca versus U/Ca relationship determined by reduced major axis regression. Parentheses indicate $\pm 2\sigma$. Sr/Ca and U/Ca are significantly correlated in all of these corals.

^bPalau 168 and 169 (Nikko Bay) and Palau 221 and 229 (Uchelbeluu) were grouped together to calculate Sr-U.

The theoretical basis for Sr-U thermometry is derived from the general relationships predicted by the model (Figure 3), which are consistent with coral data (Figures 4 and 5). Yet, it is critical to recognize that Sr-U is empirically regressed against temperature in a core-top calibration, which has two important implications for its application to corals outside of our calibration data set. First, seasonal temperature variability likely contributes, in part, to coral Sr/Ca signals, so that the regression line fit between Sr/Ca and U/Ca for a particular coral (equation (1)) captures this seasonal temperature variability in Sr/Ca in addition to variability imposed by vital effects. For this reason, Sr-U as defined here is correlated with mean annual temperature and cannot yet be applied to reconstruct seasonal temperature variability. Second, we have defined Sr-U over the temperature range 26°C to 30°C based on approximately monthly sampling of *Porites* skeletons for Sr/Ca and U/Ca ratios calibrated with the JCP-1 coral standard. Existing Sr/Ca and U/Ca data sets from *Diploria* and *Porites* corals collected in the Atlantic and Pacific basins show correlations and slopes between these two ratios that are similar to those found in our 14 corals (Table 1), suggesting that the link between Sr/Ca and U/Ca is a consistent feature of coral skeletons. However, only corals analyzed in this study are used to calibrate Sr-U to temperature because previous paired measurements of modern coral Sr/Ca and U/Ca ratios are not traceable to JCP-1. We hypothesize that Sr-U is robust to a range of conditions, but we note that its accuracy for different coral genera, timescales, and mean annual temperatures outside of our calibration data set should be validated with modern corals before application to paleoreconstructions.

Sr-U thermometry uses U/Ca ratios to account for the vital effects on Sr/Ca that are driven by the carbonate chemistry, specifically the $[\text{CO}_3^{2-}]$, of the ECF. While ECF $[\text{CO}_3^{2-}]$ may be sensitive to seawater $[\text{CO}_3^{2-}]$, our model and our coral data indicate that variability in seawater chemistry does not impact the fidelity of the Sr-U thermometer. The modeled relationship between pH_{ECF} and U/Ca is sensitive to ambient seawater chemistry (Figure 3c), but the relationships among Sr/Ca, U/Ca, and temperature—for the most part—are not (Figure 3b). Since the start of the industrial era, anthropogenic emissions have increased atmospheric CO_2 from ~280 to ~400 ppmv, which has decreased seawater $[\text{CO}_3^{2-}]$ by ~40 $\mu\text{mol kg}^{-1}$ [Feely et al., 2009]. Our model predicts that this $[\text{CO}_3^{2-}]$ change alone has a negligible effect, less than 0.03°C, on the accuracy of Sr-U thermometry (Figure 3), because it is mostly overridden by changes within the coral ECF. In fact, the corals used in this study were collected from reefs spanning a range of seawater carbonate chemistry [DeCarlo et al., 2015b], including a twofold difference in $[\text{CO}_3^{2-}]$ from 141 $\mu\text{mol kg}^{-1}$ in the bays of Palau to 290 $\mu\text{mol kg}^{-1}$ in the Red Sea [Shamberger et al., 2014; Bernstein et al., 2016]. Despite this wide range,

residuals of the Sr-U temperature calibration are not significantly correlated with seawater $[\text{CO}_3^{2-}]$ ($r^2 = 0.01$), further highlighting that Sr-U is largely robust to changes in ambient seawater carbonate chemistry.

3.3. Implications for Coral Paleothermometry

Coral paleothermometry began with the discoveries that seasonal cycles of $\delta^{18}\text{O}$ and Sr/Ca correlate with seawater temperature [Weber and Woodhead, 1972; Smith et al., 1979]. The application of $\delta^{18}\text{O}$ as a direct temperature proxy is limited by its sensitivity to salinity, leaving Sr/Ca as the preferred temperature proxy. However, once temperature calibrations were developed for many different corals collected across the tropics, it became clear that a single relationship between temperature and Sr/Ca does not exist [Corrège, 2006]. A variety of approaches have been undertaken to resolve the nontemperature controls on coral Sr/Ca ratios, including sampling along maximum growth axes [de Villiers et al., 1994], empirically regressing temperature to a variety of element ratios [Quinn and Sampson, 2002], correcting with coral growth rate [Saenger et al., 2008], accounting for “biosmoothing” [Gagan et al., 2012], and replicating time series [DeLong et al., 2013]. However, no one approach has been able to resolve all of the Sr/Ca vital effects, and Sr/Ca-based reconstructions continue to be plagued with unexplained decouplings from temperature [Wu et al., 2014].

Here we present a new coral paleothermometer developed from a bottom-up approach. Laboratory experiments were used to evaluate the temperature and carbonate chemistry controls of aragonite Sr/Ca and U/Ca ratios, in the absence of any influence from the coral polyp [DeCarlo et al., 2015a]. The abiogenic partitioning results were then placed within the framework of a biomineralization model to understand how corals influence these element ratios while building their skeletons. Importantly, the model makes testable predictions of the relationships among coral skeleton Sr/Ca and U/Ca ratios, and pH_{ECF} (Figure 3), even though there are no correlations among these variables in experimentally precipitated abiogenic aragonite [DeCarlo et al., 2015a]. These predictions are borne out in the composition of coral skeletons collected from different reefs across the Pacific Ocean and the Red Sea (Figures 4 and 5). The agreement between the model predictions and the coral data shows that by combining information from Sr/Ca and U/Ca ratios, we are capturing the essential aspects of the biomineralization process that influence the elemental composition of the skeleton.

Sr-U offers a new approach to coral paleothermometry that is based on our understanding of the biomineralization process. Coral Sr/Ca ratios are sensitive to temperature, but that influence is subordinate to vital effects, which produce a range of Sr/Ca-temperature relationships (Figure 3). With the Sr-U thermometer, we incorporate information from two element ratios that are sensitive to different aspects of the biomineralization process—Sr/Ca, which is sensitive to temperature but also influenced by vital effects and U/Ca which records vital effects but is insensitive to temperature. In this way, U/Ca ratios can be used to normalize Sr/Ca ratios to a single temperature. Sr-U thermometry combines the temperature sensitivity of Sr/Ca with the vital effect sensitivity of U/Ca to extract temperature information from coral skeleton with accuracy not obtained by any other geochemical approach (Figure 5).

The utility of a temperature proxy is judged on its ability to provide accurate temperature information prior to the beginning of instrumental records. Currently, reconstruction of SST several centuries or more into the past is performed using Sr/Ca calibrations developed with modern corals and applied to fossil samples [DeLong et al., 2010; Hereid et al., 2013; Toth et al., 2015]. This approach is subject to significant uncertainty as a result of the wide variability in Sr/Ca-temperature relationships derived from coral colonies living at the same temperatures (Figure 4). For this reason, Sr-U thermometry may prove particularly valuable for predicting SST from fossil corals that lack a modern calibration period. The ability of the Sr-U thermometer to accurately predict absolute temperature from different corals with a single calibration equation, applicable over a broad spatial scale, separates it from thermometers based on Sr/Ca alone.

Proxy reconstructions of past climate variability assume that the relationship between the proxy and the climate variable of interest is constant with respect to space and time. Coral Sr/Ca paleothermometry violates this assumption due to the influence of vital effects on Sr/Ca-temperature relationships within the skeleton of single colonies. Decoupling (or “breakdown”) of the relationship between Sr/Ca and SST has been observed in several studies [Marshall and McCulloch, 2002; Felis et al., 2009; Wu et al., 2014]. Perhaps the most drastic Sr/Ca breakdown was observed by Felis et al. [2009], in which Sr/Ca ratios of a coral from the northwest Pacific implied that 1995–2000 was the coolest period of the twentieth century, when in fact it was the

warmest. Critically, this Sr/Ca breakdown is accompanied by a positive correlation with U/Ca ratios [Felis *et al.*, 2009]. Our model explains this breakdown: corals may shift along the Sr/Ca and U/Ca trajectory driven by vital effects, even in the absence of temperature changes (Figure 3). The positive correlation between Sr/Ca and U/Ca reported by Felis *et al.* [2009] suggests that observed Sr/Ca breakdowns are actually temporal variations in the coral biomineralization process. This likely explains why many existing Sr/Ca records diverge from instrumental SST [Grove *et al.*, 2013; Storz *et al.*, 2013; Wu *et al.*, 2014] and potentially influences Sr/Ca records extended prior to the instrumental record for which no independent, direct observations of SST are available for comparison. When Sr/Ca breakdowns are observed during recent decades, instrumental SST allows us to identify that the Sr/Ca thermometer failed [Felis *et al.*, 2009; Grove *et al.*, 2013; Storz *et al.*, 2013; Wu *et al.*, 2014]. It is important to recognize, however, that when Sr/Ca is extended into the paleorecord, a Sr/Ca breakdown cannot be distinguished from a true temperature change unless coupled with U/Ca ratios to calculate Sr-U.

4. Conclusion

Coral skeletons are promising archives for high-resolution reconstructions of climate changes in the ocean over the past several millennia. However, application of geochemical temperature proxies—such as Sr/Ca—has proven difficult due to the confounding influence of physiological vital effects. Here we present a new coral paleothermometer, Sr-U, which uses U/Ca ratios to account for the influence of vital effects on Sr/Ca-temperature relationships. This approach significantly improves the accuracy of reconstructed temperature from coral skeleton. We calibrated Sr-U to temperature using a new data set of Sr/Ca and U/Ca ratios measured in 14 corals collected in the Pacific Ocean and the Red Sea spanning a mean annual temperature range of 26°C to 30°C. Sr-U thermometry has a standard deviation of prediction of only 0.5°C, which is twice the accuracy compared to using Sr/Ca alone. Coral skeleton Sr/Ca and U/Ca ratios are routinely measured by ICP-MS, making the Sr-U thermometer readily available to perform temperature reconstructions. With the improved accuracy and applicability of a single calibration equation to individual corals collected from different locations, Sr-U thermometry has great potential for extending our limited instrumental temperature records in the ocean.

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